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THE TRIBOLUMINESCENCE OF ZINC CADMIUM SULFIDE

Carmen M. Cialella
James G. Dante

November 1978

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
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A fuze system utilizing semi-conductor technology and triboluminescence (TL) has been designed and tested. This report presents subsequent efforts to determine the light output of the TL phosphor, Zinc Cadmium Sulfide (ZnCdS) as a function of bonding resin, substrate material (steel and aluminum), phosphor thickness, impact velocity, and temperature. Several bonds were tested and one was selected for future investigation.

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I. INTRODUCTION

Triboluminescence (TL) may be defined as the emission of light through the mechanical disruption of crystals. This phenomenon has been known and studied by scientists for several hundred years. The exact nature of the luminescence mechanism is not yet fully understood. However, triboluminescence is thought to be generated by mechanical stress cycling or by fracture. Recent studies by Meyer, et al[1] and Chudacek[2] show that the TL spectrum of Zinc Sulfide (ZnS) single crystals is the same as the fluorescence spectrum due to x-ray bombardment. This indicates that the light emission from both mechanisms has a common origin. The ZnS spectrum peaks at a wavelength of approximately 580 nanometers (nm) and is fairly broad with a half width of about 50 nm. Chudacek[3,4] conducted other studies of the periodic excitation and kinetics of TL, principally of ZnS, although other materials were examined. G. Alzetta, et al[5] examined the excitation of TL by deformation of single crystals of ZnS (Mn) and other materials. Sodomka[6] determined that the TL intensity follows the frequency of a periodic change in pressure by impact and that the brightness pulse was produced only when the pressure pulse decreased and that it reached maximum when the pressure pulse was minimum. Zink, et al[7] determined that the TL of sugars is not a function of crystal size. He is investigating the possibility of adding impurities or activators in TL materials to increase the light output and/or change the spectral distribution of the emitted light.

Zink[8] also measured the triboluminescence and photoluminescence spectra of our ZnCdS phosphor (Dupont 1200 Phosphor). These spectra are shown in Figures 1 and 2. He notes that the triboluminescence spectrum peaks at about 530 nm and that the photoluminescence spectrum peaks at about 545 nm. He further states that these spectra are uncorrected for instrument response and that the difference between the two peak maxima may be caused by the effect of pressure in addition to the small instrument response difference (about 5 nm). The triboluminescence spectrum was produced by grinding the ZnCdS phosphor.

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[1] *K. Meyer and D. Obrikat, Z. Phys. Chem. 240, 309 (1969).*

[2] *I. Chudacek, Czeck J. Phys. 17, 34 (1967).*

[3] *I. Chudacek, Czeck J. Phys. 15, 359 (1965).*

[4] *I. Chudacek, Czeck J. Phys. B 17 (1967).*

[5] *G. Alzetta, I. Chudacek, and R. Scarmozzins, phys. stat. sol. (a) 1, 775 (1970).*

[6] *L. Sodomka, Czeck J. Phys. B 14 800 (1964).*

[7] *Jeffrey I. Zink, Gordon E. Hardy, and James E. Sutton, Journal of Physical Chemistry, 80, 248 (1976).*

[8] *Jeffrey I. Zink, Private Communication.*

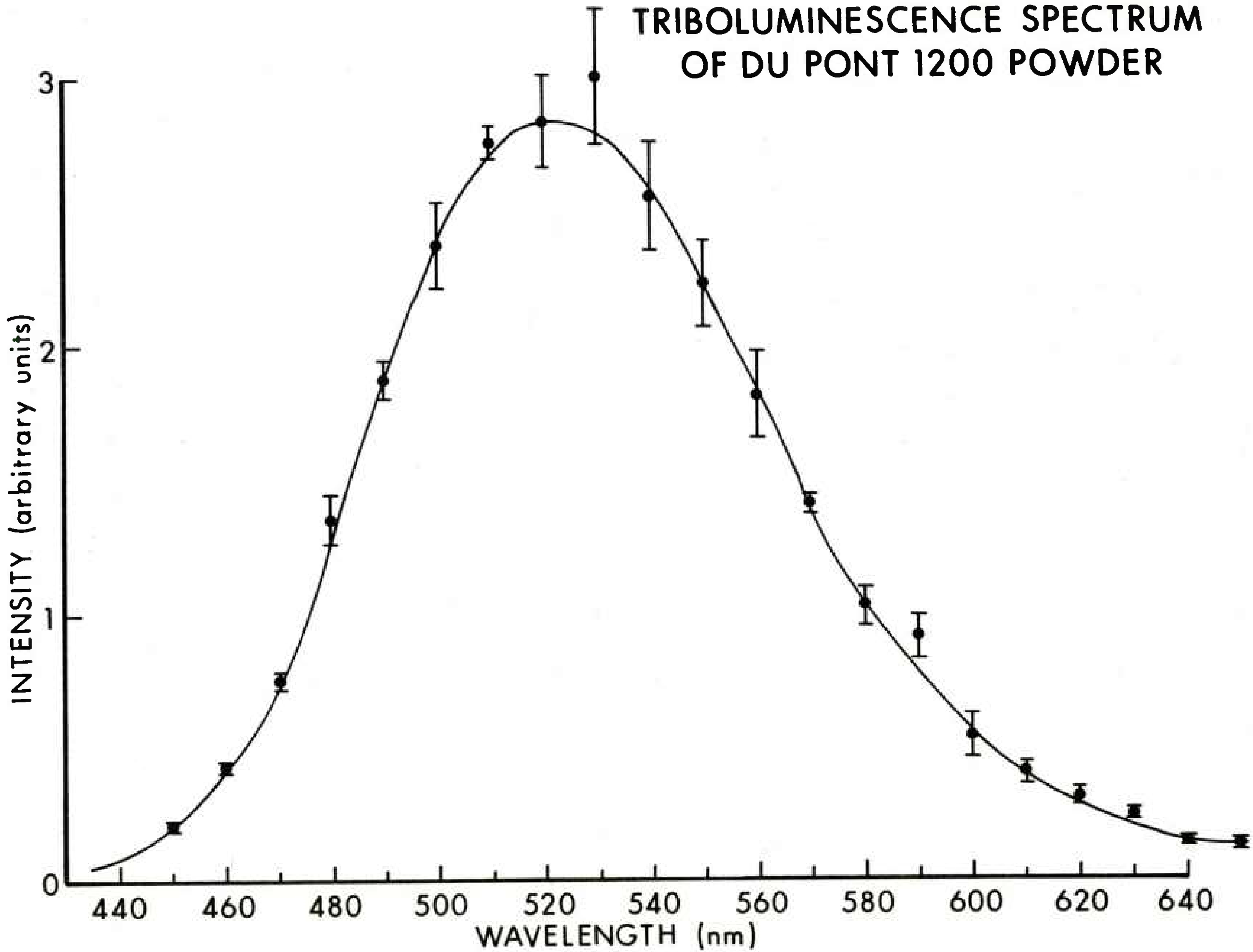

Figure 1. Iriboluminescence Spectrum of Dupont 1200 Phosphor (Zink)

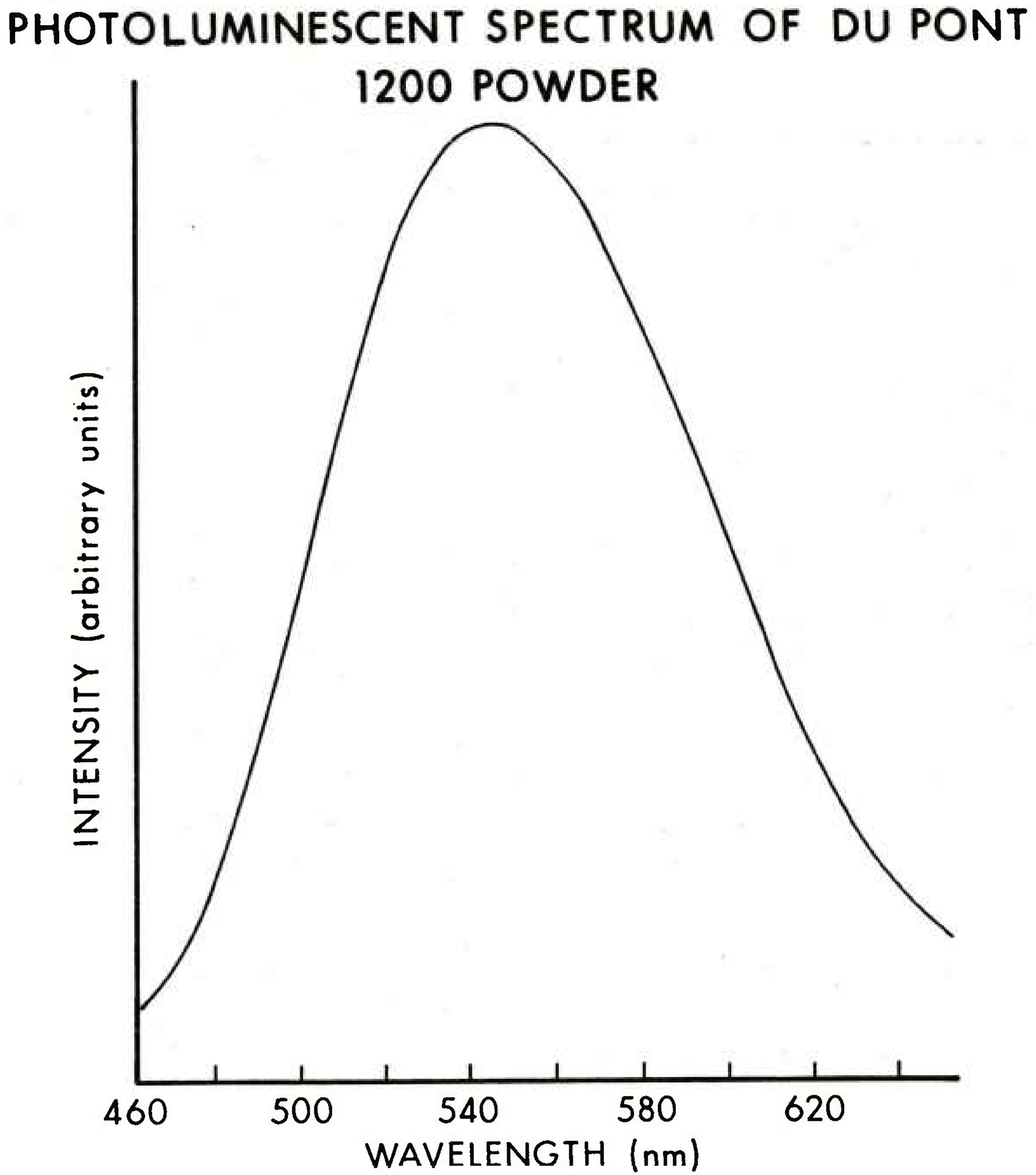

Figure 2. Photoluminescence Spectrum of Dupont 1200 Phosphor (Zink)

In work partly supported by this laboratory, Djordjevic[9] also measured the triboluminescence spectrum and the Roentgenoluminescence (x-ray excitation) spectrum of samples of our ZnCdS phosphor. These spectra are shown in Figures 3 and 4. Both spectra peak at about 540 nm. However, he did find about a 15 nm difference in the spectral peaks of Dupont D-Screen (ZnS:Ag) with the photo-peak higher as did Zink (the tribopeak was located at about 460 nm; the photopeak at about 475 nm). He also attributes the difference to pressure effects. The triboluminescence spectra were obtained by impact. It therefore may be reasonably concluded that the triboluminescence spectrum of ZnCdS peaks at about 535 nm with a possible error of about 10 nm.

Djordjevic concludes that triboluminescence caused by the mechanical deformation of a solid cannot be simply assigned to a unique mechanism. The complex energy band structure of imperfect crystals allows a multitude of excitation and relaxation processes. However, it appears that triboluminescence emission is comparable to other well documented and better understood luminescence phenomena. The difference is in the process of excitation of electrons, while relaxation with photon emission involves the same optical transition centers as in other types of luminescence.

In this study five inorganic TL materials were initially investigated:

Zinc Fluoride: Manganese activated (ZnF_2: Mn)

Zinc Sulfide: Silver activated (ZnS: Ag)

Zinc Sulfide: Manganese activated (ZnS: Mn)

Calcium Pyrophosphate: Dysprosium activated (CaP_2O_7: D_4)

Zinc Cadmium Sulfide (ZnCdS).

It was determined that zinc-cadmium-sulfide (ZnCdS) produced the highest TL light output of the five inorganic materials tested; therefore all of the TL investigations reported here are of ZnCdS. The initial source of ZnCdS was Dupont Cronex x-ray fluoroscopic screen, type CB-2. A later source of ZnCdS, used in this work, was in the form of a fine yellow powder (Dupont 1200 Phosphor).

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[9] *Borislav Boro Djordjevic, "Triboluminescence," Master of Science Thesis, The Johns Hopkins University, February 1978.*

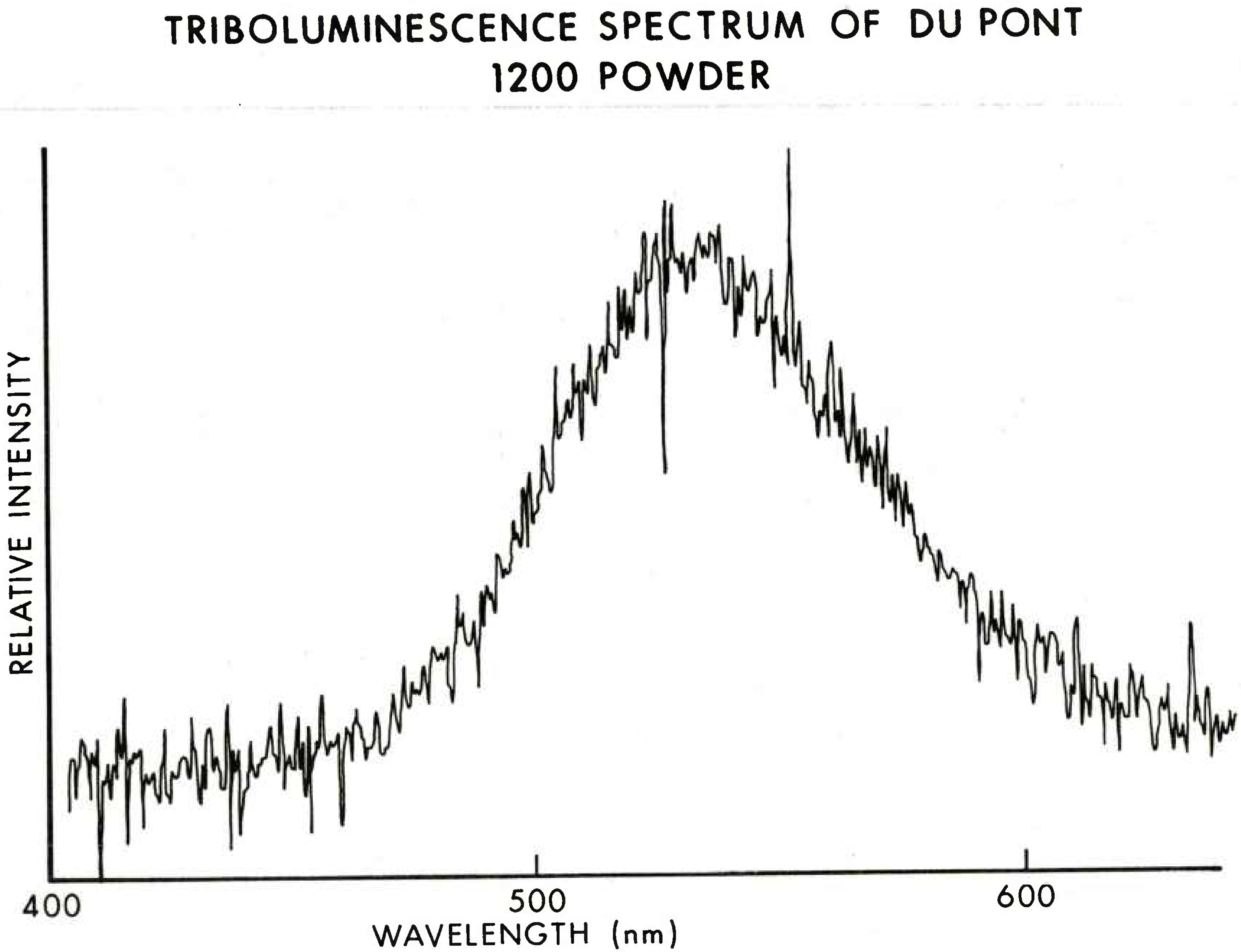


Figure 3. Triboluminescence Spectrum of Dupont 1200 Phosphor (Djordjevic)

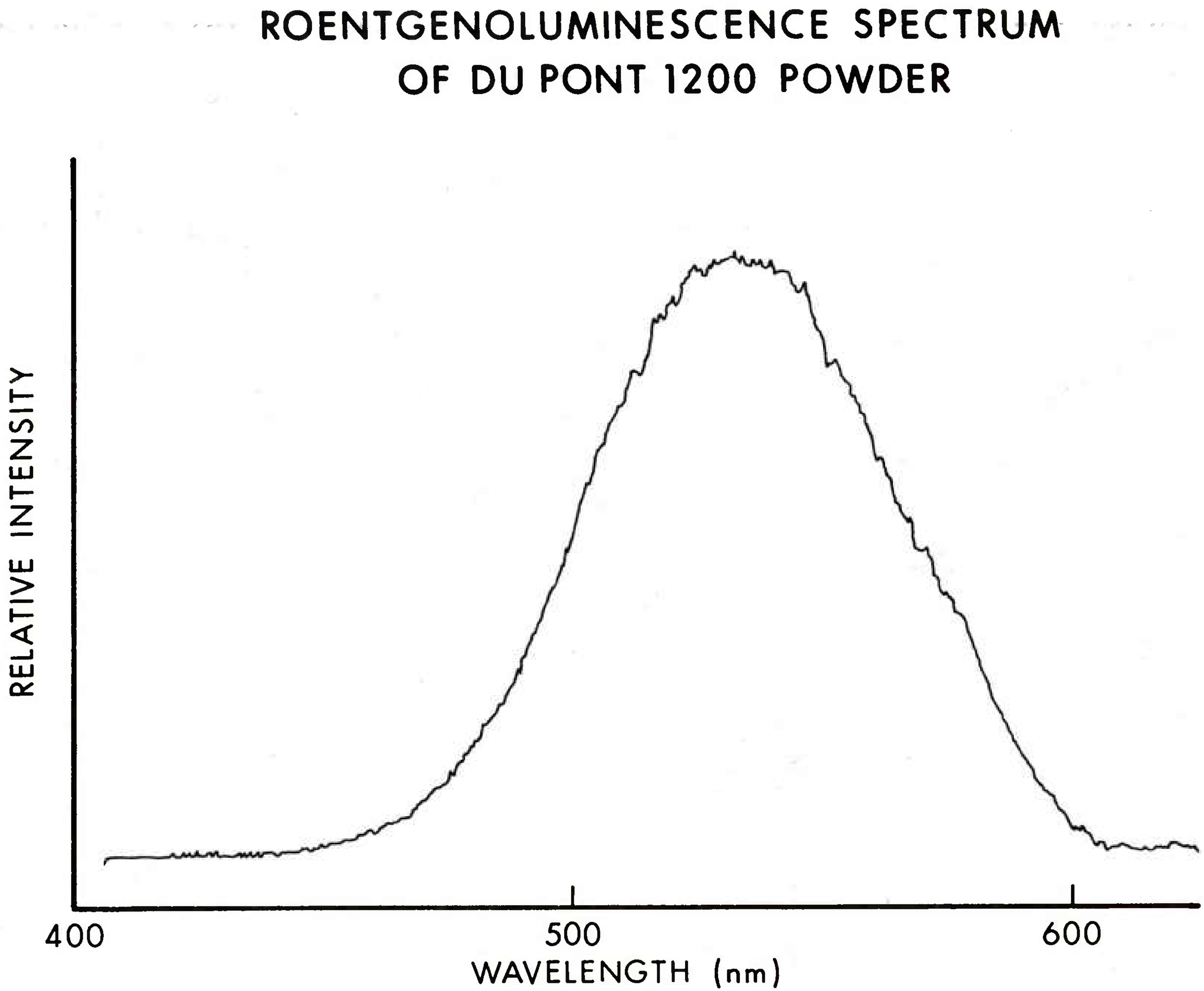


Figure 4. Roentgenoluminescence Spectrum of Dupont 1200 Phosphor (Djordjevic)

The overall purpose of this work is to apply the TL concept to a wireless fuze system for army warheads. The concept was tested in several prototype 66mm Law warheads and proved successful[10,11]. This report presents subsequent efforts to determine the light output of the TL phosphor (ZnCdS) as a function of:

A. Bonding resin;

B. Thickness of phosphor;

C. Substrate material (steel and aluminum);

D. Impact pressure (projectile velocity);

E. Temperature.

The principal objective of the work reported here was to bond the 1200 phosphor to either aluminum or steel, maintain a high light output on impact, and assure that the bonded system be sufficiently durable to pass military standard environmental and performance tests.

II. EXPERIMENTAL SET-UP

Figure 5 is a diagram of the impact set-up for the light testing of the TL of ZnCdS. The bore diameter of the air gun was 2.54 cm. The projectiles were 2.52 cm diameter aluminum or polypropolux, 5.08 cm long with a steel tip 0.635 cm long (2.40 cm dia). A laser beam with photodetector was used to determine the velocity of the projectile and to trigger the oscilloscope. All samples were 6.35 cm squares mounted in a specimen holder made of 1.25 cm thick steel plates. The steel specimens were 1.6mm thick and the aluminum specimens were 0.8mm thick. The projectiles impacted the uncoated side of the specimen.

A Dumont 6292 photomultiplier tube (PMT) was used to quantitatively measure the light output of the ZnCdS. The PMT was placed 24.4 cm from the target specimen at an angle of 45° from the line of flight of the projectile. The PMT was calibrated by measuring the output voltage as a function of irradiance. The light was provided by an incandescent source filtered to match the peak of the TL spectrum emitted by the ZnCdS (wavelength about 540 nm, bandwidth about 10 nm). Figure 6 presents the calibration plot of PMT output voltage vs irradiance used in these measurements.

---

[10] *Glass, C., Dante, J., Cialella, C., Golaski, S., "An Electro-Optical Fuze System," BRL MR 2552, October, 1975.* (AD #B008043L)

[11] *Glass, C., Dante, J., Cialella, C. Golaski, S., "A Light Activated Fuze System," BRL MR 2726, February 1977.* (AD #B017049L)

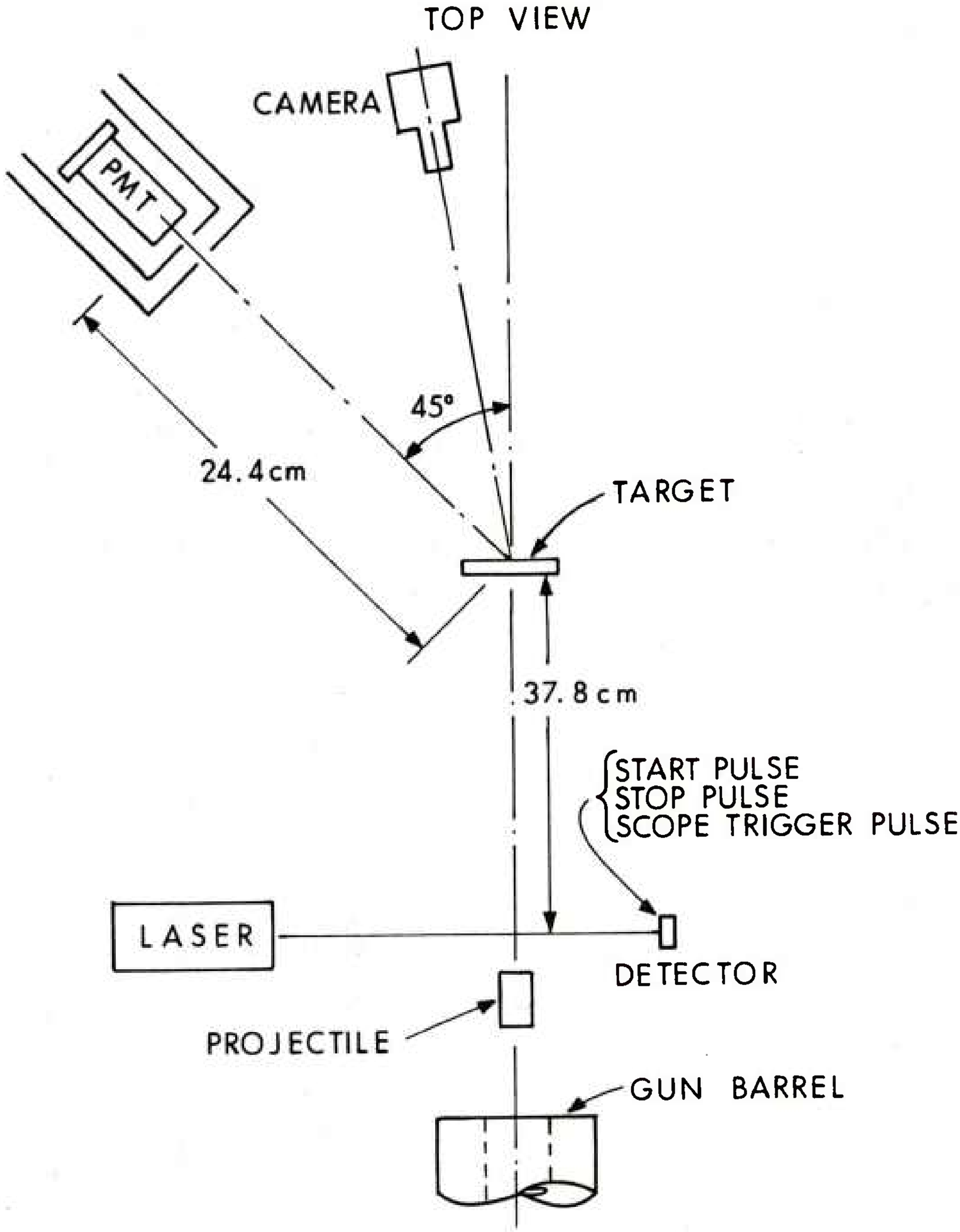


Figure 5. Diagram of the Impact Set-Up for Testing Triboluminescent Materials

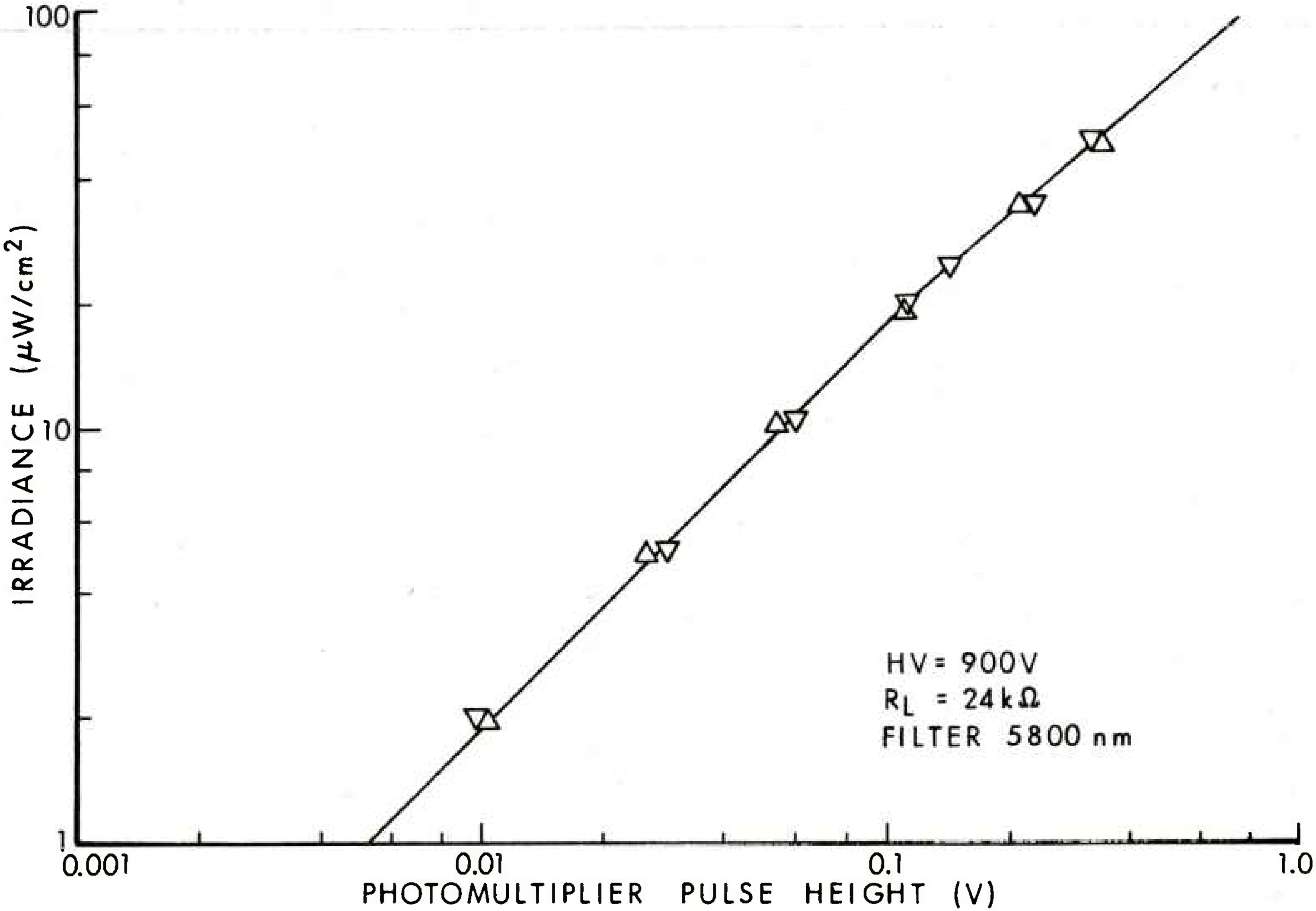


Figure 6. Photomultiplier Calibration Curve

A camera was mounted at an angle of approximately 25° from the line of flight of the projectile about 60 cm above the height of the target. Using Polaroid recording film ASA 10,000 with an open shutter, the light output of the TL ZnCdS specimens upon impact were photographed. Figures 7 and 8 show typical results from both the PMT and the camera for a single impact. Figure 7 shows the data for an aluminum-backed specimen and Figure 8 shows the data for a steel-backed specimen.

III. RESULTS

A. Light Output of Dupont CB-2 X-Ray Fluorescence Screen

To check the operation of the test equipment the light output of Dupont CB-2 x-ray fluorescence screen produced by impact was measured with each set of sample measurements. The results of over fifty measurements showed the light output at the detector to be 36 $\mu W/cm^2$ with a standard deviation of 5 $\mu W/cm^2$ over a range of projectile velocities of from about 80 m/s to 280 m/s. These data are plotted in Figure 9. Earlier data produced with a pneumatic cylinder piston impactor with a maximum velocity of five m/s are included. These data were normalized to the distance of 24.4 cm at which the rest of the measurements were made.

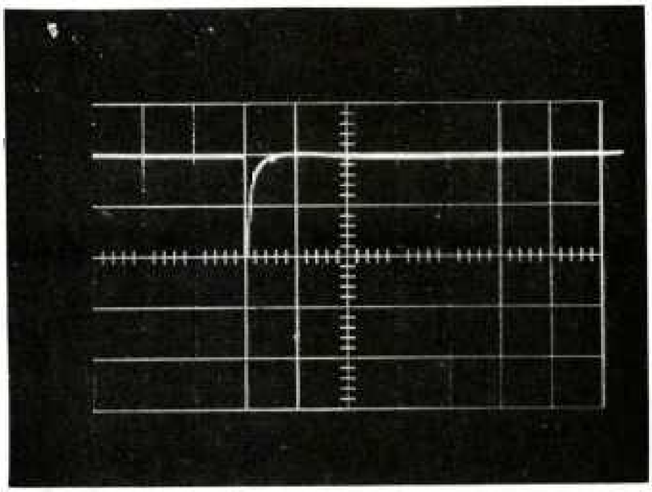
There appears to be a correlation between projectile velocity and light output at very low velocities; however, above at least 50 m/s the light output is constant out to about 300 m/s within the experimental uncertainties of the measurements.

B. Light Output of Marvalaud Specimens

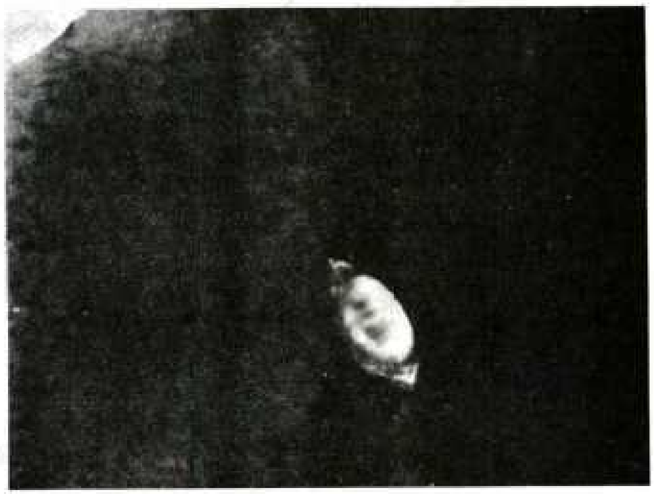
1. Effects of Phosphor Thickness. A number of specimens consisting of ZnCdS phosphor (Dupont 1200) bonded to both steel and aluminum substrates was provided by the Marvalaud Corporation (Westminster, Maryland). Each set of specimens contained a different bond or a variation of the same bonding material. Two sets of specimens identified as No. 6 and No. 9 produced the highest light output under impact. These specimens were coated with a phosphor thickness of approximately 100 mg/cm^2 (about the same thickness as the CB-2 screen). This is really weight per unit area, which is proportional to thickness, and for simplicity it will be called thickness. In order to determine the light output as a function of thickness, specimens were requested using No. 6 and No. 9 bonds, coated with phosphor thicknesses of 50, 100, 200, 300, 400 and 500 mg/cm^2 respectively on both steel and aluminum substrates. The actual phosphor thicknesses provided were 77, 129, 181, 233, 284 and 336 mg/cm^2.

Figure 10 shows the results obtained from the measurements of the light output of the series 6 bonded specimens as a function of phosphor thickness. The projectile velocities were approximately 250 m/s. Several observations are listed concerning these results:

IMPACT TEST RESULTS OF ZnCdS BONDED TO ALUMINUM SUBSTRATE DENSITY : 284 mg/cm^2



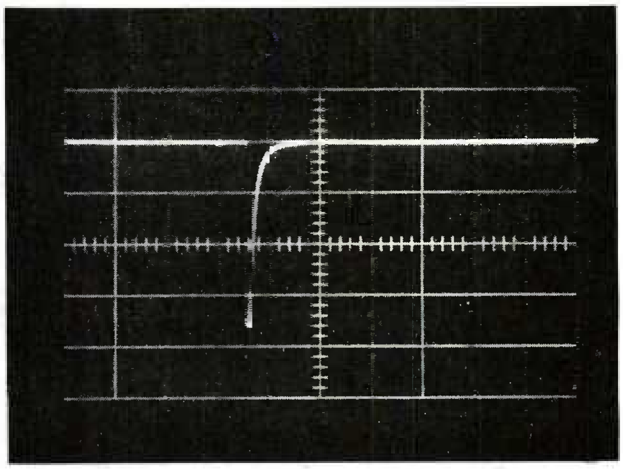
A. PHOTOMULTIPLIER OUTPUT
SWEEP : 0.5 ms/cm
SENSITIVITY : 0.1 V/cm
IRRADIANCE : 33 $\mu W/cm^2$



B. OPEN SHUTTER CAMERA VIEW OF IMPACT

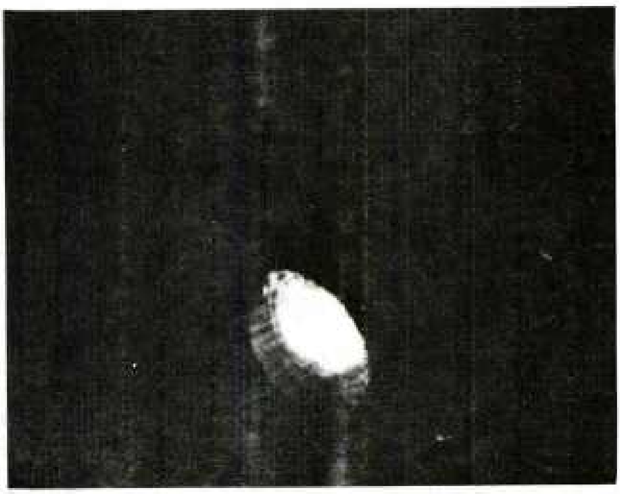
Figure 7. Typical Impact Test Results of ZnCdS Powder - Aluminum-Backed Specimen

IMPACT TEST RESULTS OF Zn Cd S POWDER
BONDED TO STEEL SUBSTRATE
DENSITY : 284 mg / cm²



A. PHOTOMULTIPLIER OUTPUT

SWEEP : 0.5 ms/cm
SENSITIVITY : 0.1 V/cm
IRRADIANCE : 53.5 μW/cm²



B. OPEN SHUTTER CAMERA
VIEW OF IMPACT

Figure 8. Typical Impact Test Results of ZnCdS Powder - Steel-Backed Specimen

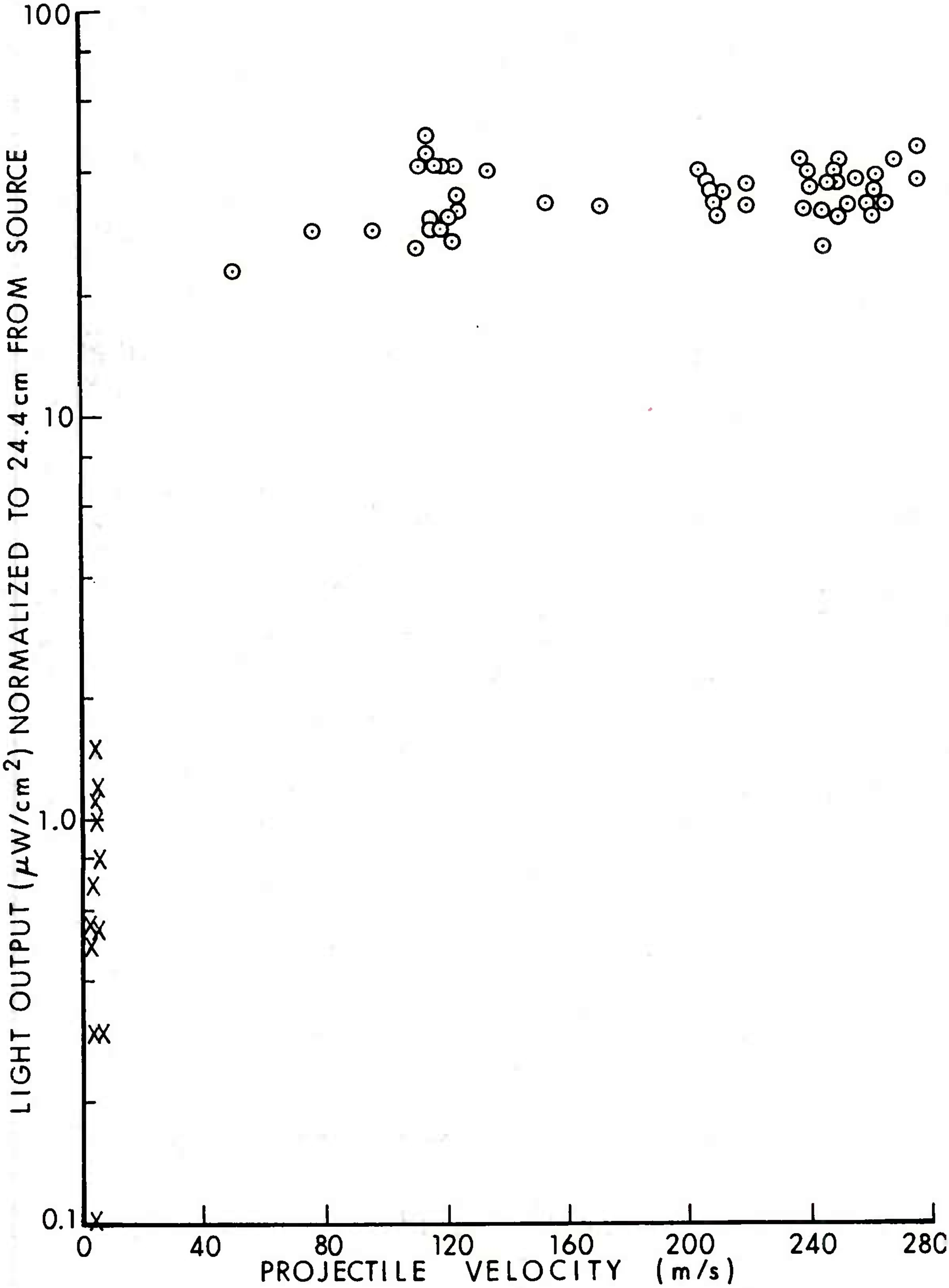


Figure 9. Light Output of Unmounted Dupont Cronex X-Ray Screen - Type CB2 vs Projectile Velocity

LIGHT OUTPUT VS
PHOSPHOR THICKNESS

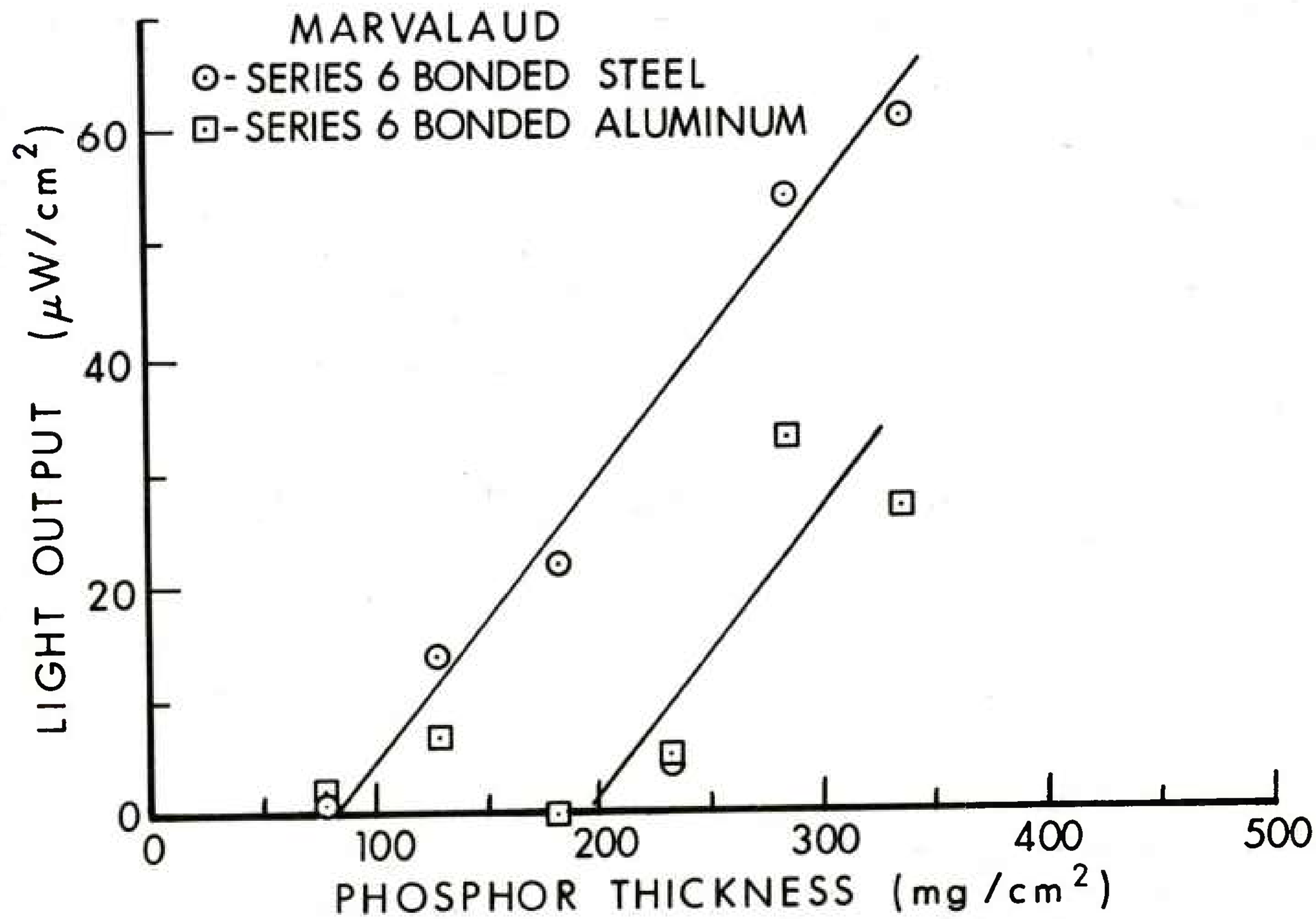


Figure 10. Light Output vs Phosphor Thickness (No. 6 Bond on Steel and Aluminum)

1. The light output is proportional to phosphor thickness and appears to be linear.

2. The light output of the steel-backed specimens is higher than that of the aluminum-backed specimens.

3. There appears to be a threshold thickness of phosphor below which no significant light output is produced (at least under the conditions described above).

Figure 11 shows the results obtained from the series 9 bonded specimens. Here (except for two anomalous points which will be discussed in a following section) the light outputs of both the steel-backed and the aluminum-backed specimens appear to be about equal. The light output is proportional to phosphor thickness, is linear, and again a threshold phosphor thickness exists.

2. Effects of Impact Velocity. It was concluded that the series 6 bonded specimens produced the highest light output and that the investigation of impact velocity and temperature effects on light output would be made with these specimens. Therefore a suite of aluminum-backed and a suite of steel-backed specimens with a phosphor thickness of 340 mg/cm^2 were obtained (bonded with the No. 6 bond). The light output was measured as a function of projectile velocity for both suites of specimens. Figure 12 presents the results of the measurements for aluminum-backed samples. The light output appears to be lower at the lower impact velocities, then remains fairly constant, at least out to about 350 m/s velocity. Two specimens produced very little light on impact. This is most probably due to something in the bond or bonding process. These specimens were hand made and the quality control of the bonding was admittedly poor.

The effects of projectile velocity on the light output of the bond No. 6 steel-backed specimens are plotted in Figure 13. The light output is constant (within a rather large error band) as the projectile velocity increases. Again, as with the aluminum-backed samples, there were two specimens which produced very little light. Thus a general conclusion is that all three specimens (the CB2 x-ray screen, the aluminum-backed specimens and the steel-backed specimens) produce a fairly constant light output as a function of projectile velocity above some minimum velocity.

3. Effects of Specimen Temperature. The results of the light output as a function of specimen temperature are plotted in Figure 14. The range of temperatures used corresponds to the range of temperatures listed in military specifications. The light output drops at temperatures below and above ambient; however, for the intended use of this phosphor the light output is still high enough to satisfy requirements. And note that one specimen at 71°C emitted more than twice the amount of light emitted at room temperature. This was another example of the

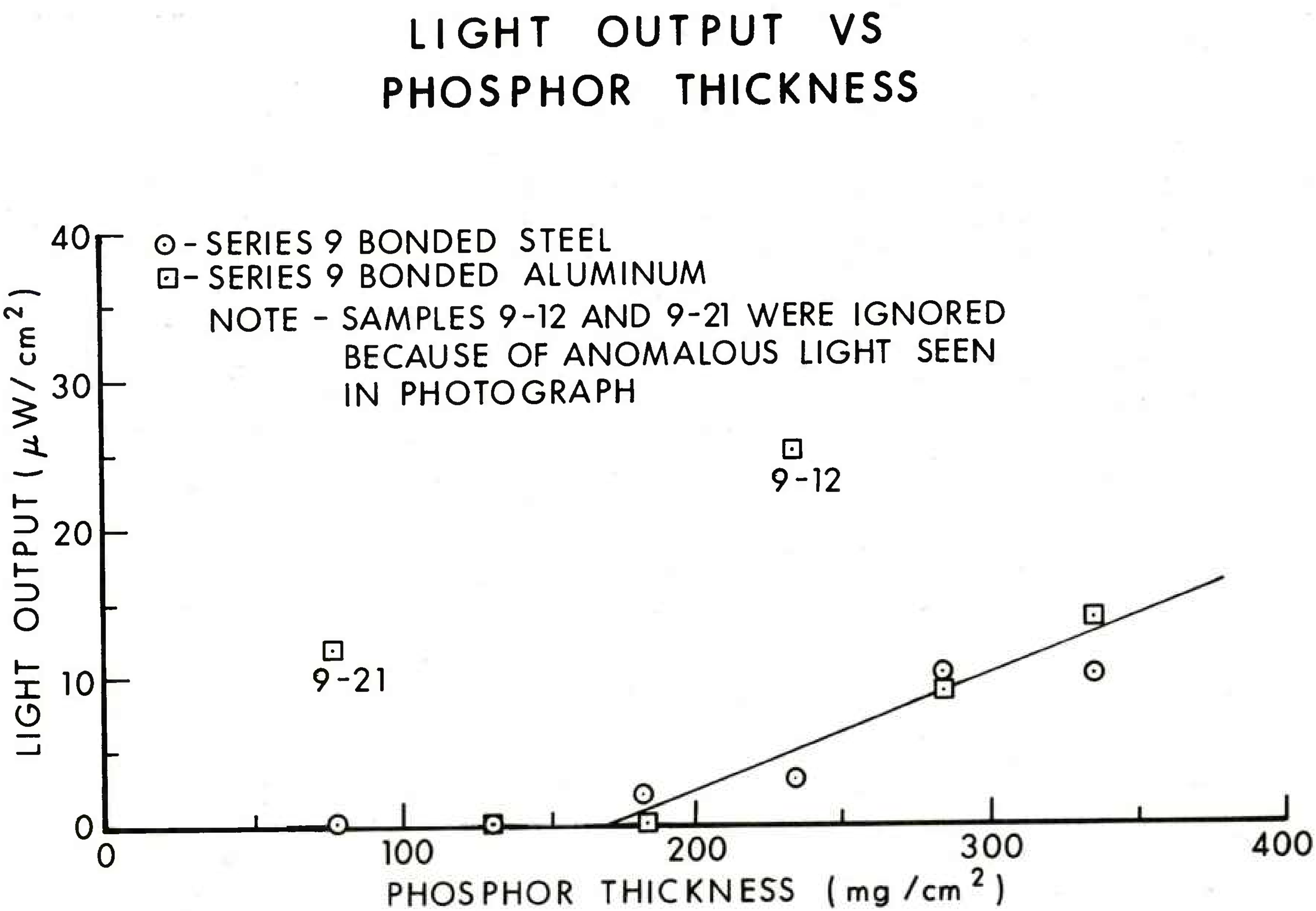


Figure 11. Light Output vs Phosphor Thickness (No. 9 Bond on Steel and Aluminum)

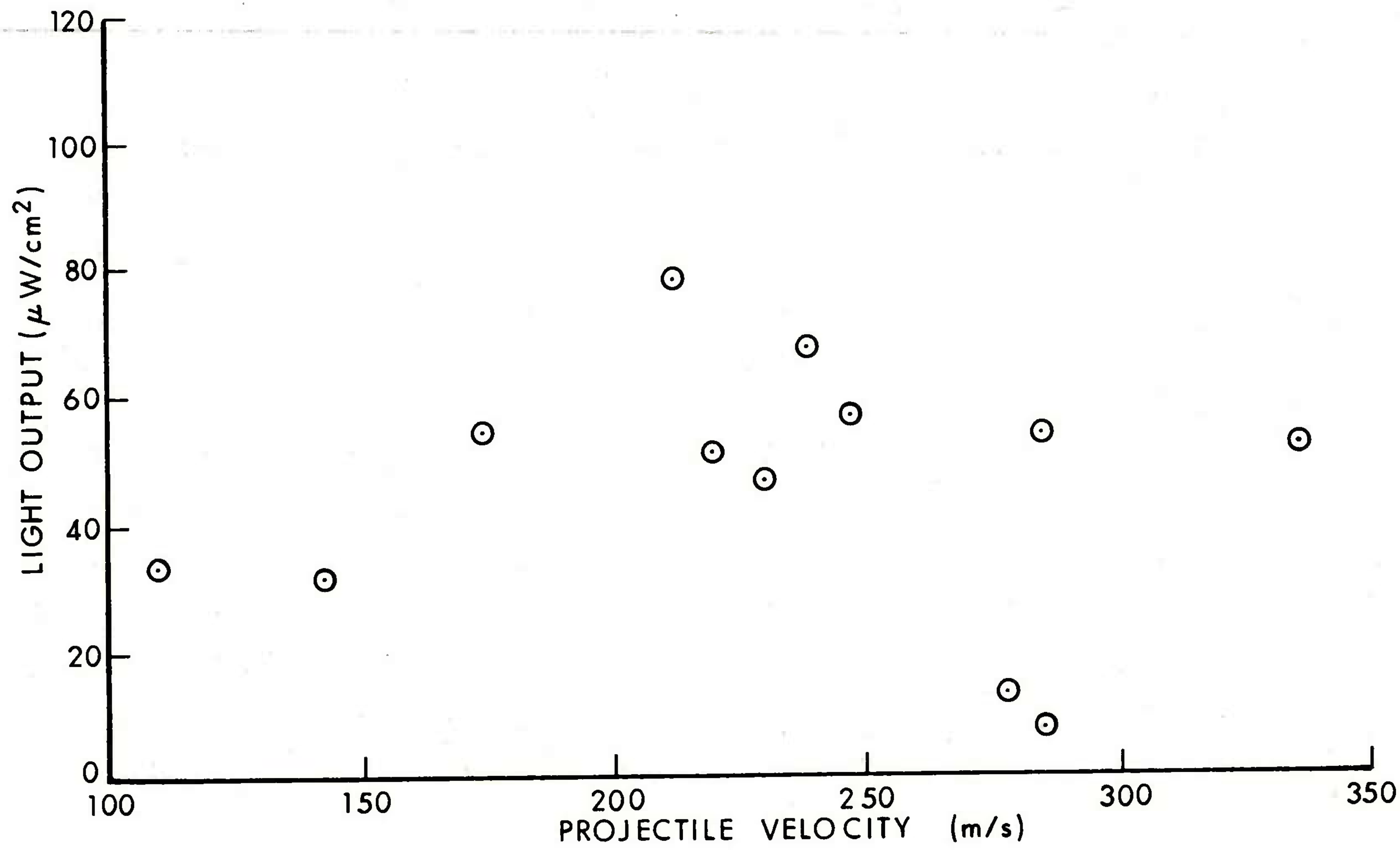


Figure 12. Light Output of Aluminum-Backed Specimens vs Projectile Velocity

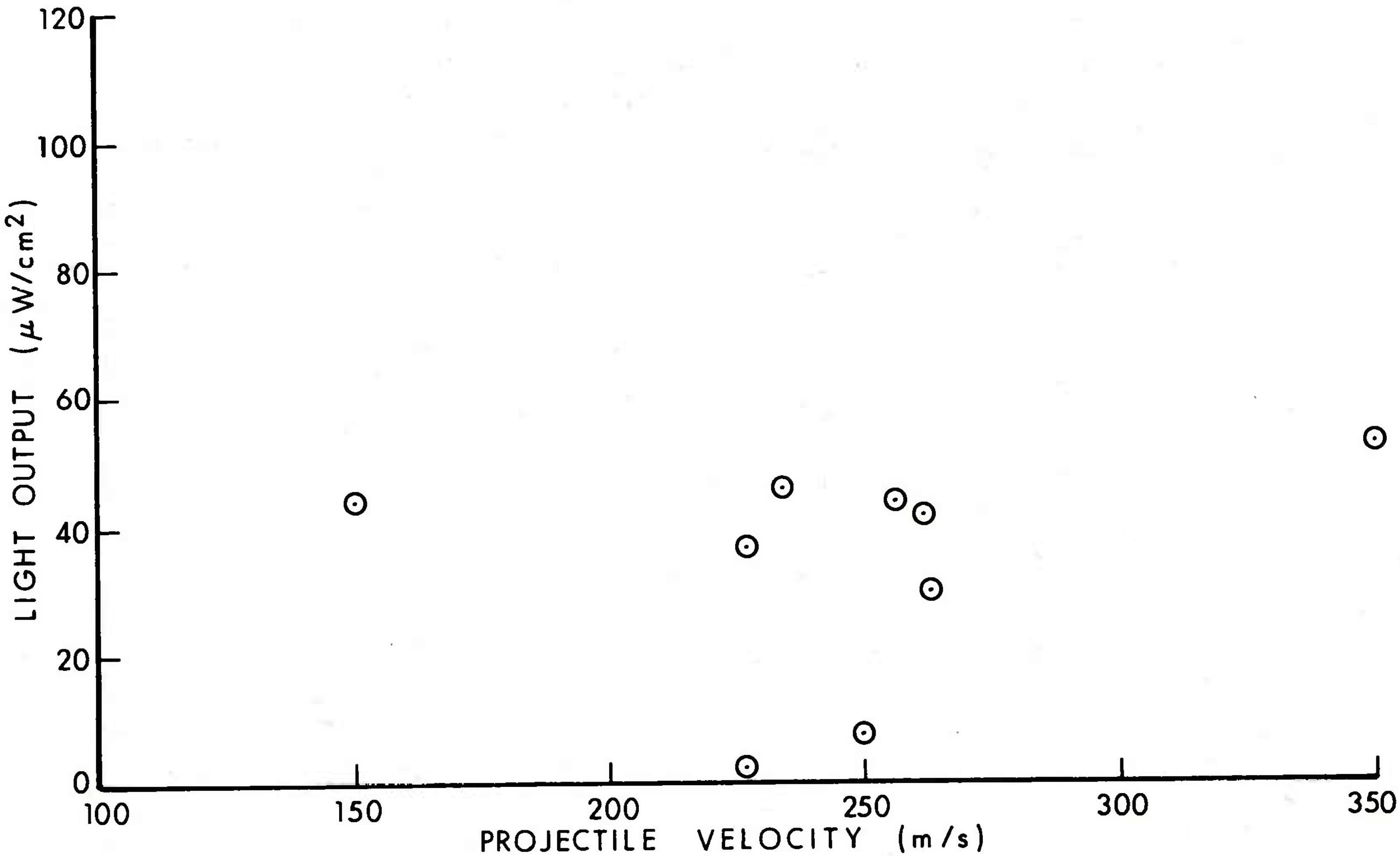


Figure 13. Light Output of Steel-Backed Specimens vs Projectile Velocity

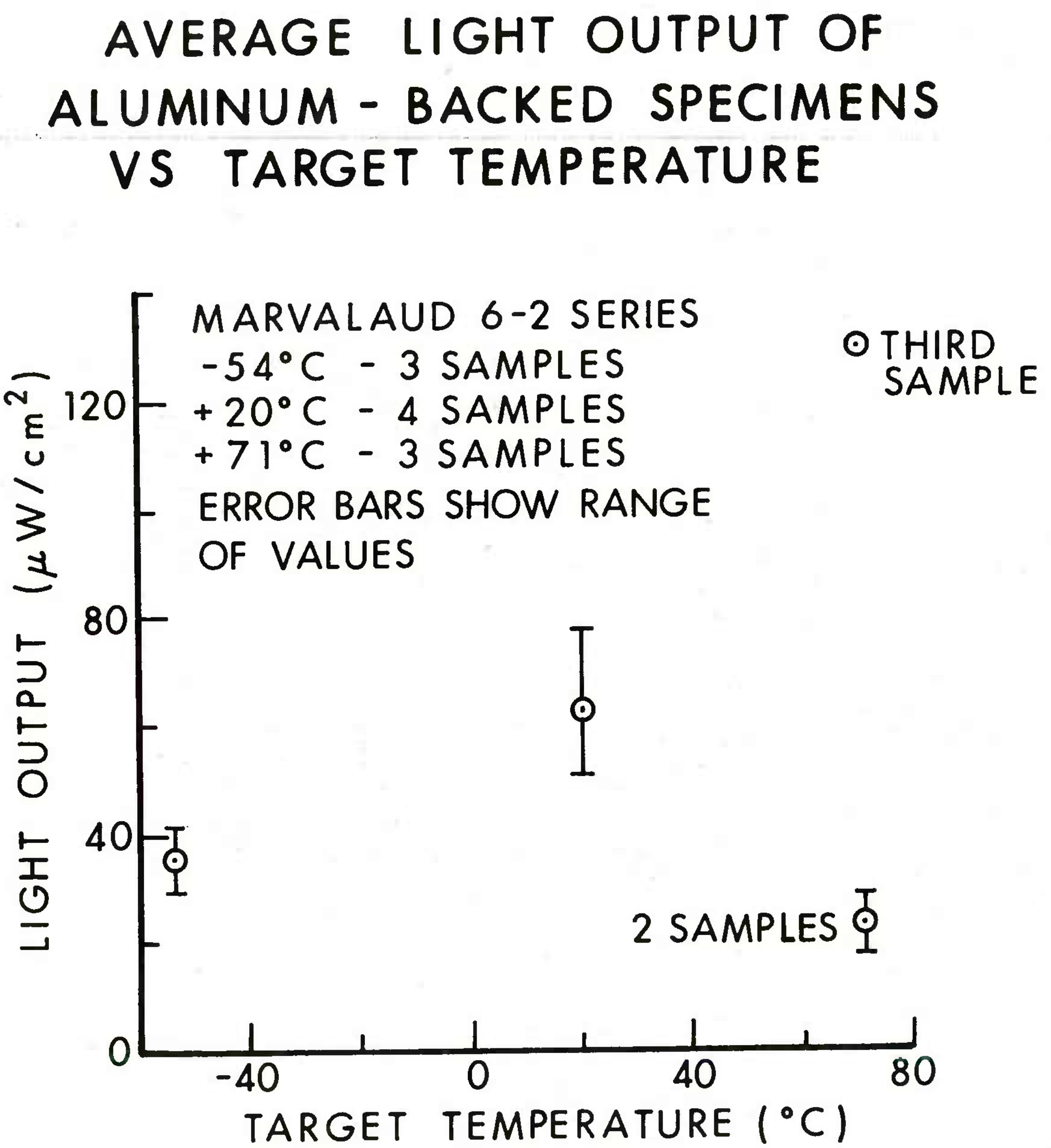


Figure 14. Average Light Output of Aluminum-Backed Specimens vs Target Temperature

"anomalous" results previously mentioned which will be discussed in the next section.

The exact cause of the decrease in light output has not been determined; however, the following possibilities are offered:

a. The luminescense spectrum shifted with temperature. This would change the sensitivity of the spectral response of the photocathode of the photomultiplier tube (spectrum changes with temperature are well documented in the literature).

b. The light output of the phosphor decreased with temperature.

c. The adhesive material was affected by the temperature change

d. Any combination of the above.

C. Extended Time Light Output (Streamers)

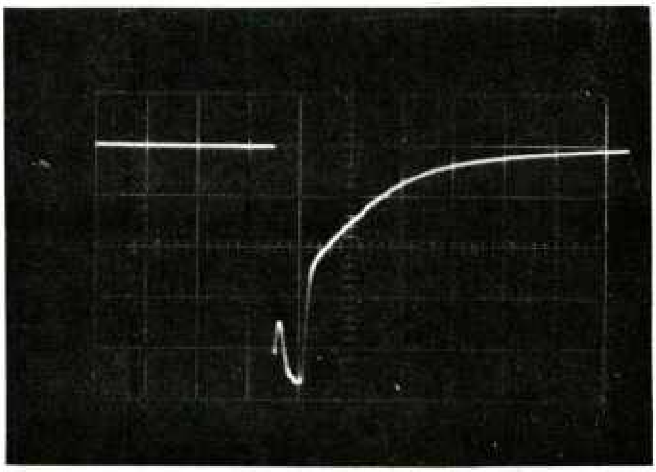
An interesting phenomenon that occurs approximately one out of ten times is that the phosphor produces light over an extended period of time, i.e., the disrupted phosphor crystals continue emitting light while in flight. We have no control over this random occurrence and as yet have no explanation for it. But the fact remains that both the PMT output pulse and the open shutter photograph confirm this occurrence. In all cases the light output of a "streamer" is much greater than the typical light output observed.

If we refer back to Figures 7 and 8, we observe that the pulse width at half maximum, of a typical light output PMT pulse is approximately 70 μs, a fairly narrow pulse. Observing the open shutter photograph we see that the camera is viewing a circular disc (remembering that the camera is positioned above and to the right of the target). This light disc is flat indicating that the light is emitted sharply at the instant of impact.

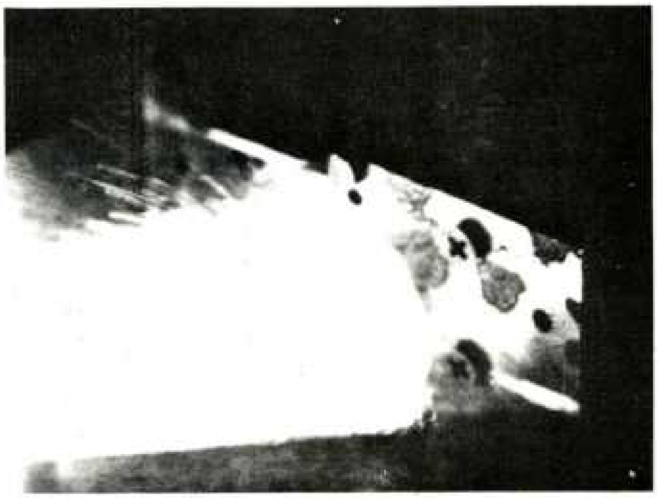
Figure 15 shows a fairly typical record of the light output of a "streamer". We first note that the PMT output pulse is double-peaked and very much broader than the pulse in Figures 7 and 8. The double peak is typical of the "streamer" pulse. The addition to the broad time width of the pulse there is also a much longer decay time. This is most probably due to the fact that the PMT is somewhat collimated and the light emitting crystals are passing through the PMT field of view.

The view from the open shutter camera dramatically illustrates the light emission of the phosphor crystals in flight and the very high intensity. The brilliance of the light output actually lights up the target holder to the extent that one can see the steel plate holder and several of the screw-heads.

IMPACT TEST RESULTS OF Zn Cd S
BONDED TO ALUMINUM SUBSTRATE
DENSITY : 340 mg / cm^2



A. PHOTOMULTIPLIER OUTPUT
SWEEP : 0.5 ms / cm
SENSITIVITY : 0.1 V/cm
IRRADIANCE : 68 μW / cm^2



B. OPEN SHUTTER CAMERA
VIEW OF IMPACT

Figure 15. Typical Impact Test Results of An Extended Time Light Output

Figure 15 states that the irradiance is 68 μW/cm^2 but it is obvious that the light is much more intense. The PMT is calibrated and the light output is determined by the height of the PMT output pulse. The more accurate procedure to determine light intensity is by integration of the area under the entire pulse. However, in the typical cases, the pulse widths are the same, so that the results that were reported (determined by the pulse height) are sufficiently accurate for the application intended.

It is interesting to note that Djordjevic also observed this phenomenon at much lower light intensities. He observed broad, double-peaked pulses from his photomultiplier output and spatial distribution of light being emitted as the phosphor has broken from its bond and is traveling through space.

IV. DISCUSSION

The second batch of specimens which were used to determine the effects of phosphor thickness on the light output showed that for the No. 9 bonded specimens the light outputs of the aluminum- and steel-backed specimens were approximately equal. However, the same set of specimens bonded with the number 6 bond showed a higher light output produced by the steel-backed specimens than for the aluminum-backed specimens. But in the third set of No. 6 bonded specimens (at 340 mg/cm^2) the aluminum-backed specimens emitted greater light intensities than the steel-backed specimens. It has been stated earlier that the quality control was very poor. It is felt that if the bonding preparation and procedure were more rigidly controlled, both the aluminum-backed and the steel-backed specimens would emit approximately the same light intensity. However, it must again be stated that under these experimental conditions, both the steel-backed and aluminum-backed specimens emitted more than enough light for the intended application of the TL phosphor concept.

One conclusion that can be made is that the preparation of the substrate material, the binding of the phosphor, the bonding of the phosphor to the substrate material, and the curing of the bond are very sensitive parameters and affect the light output of the phosphor significantly.

The experimental error (standard deviation) of these measurements is approximately ± 15 percent. In addition, the lack of bonding controls adds some unknown quantity to the experimental error. In spite of these errors the trends of the TL output of bonded ZnCdS as a function of thickness, impact velocity, substrate material and temperature have been shown and may be of interest to other investigators of this phenomenon.

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